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(71) Applicant

Research Development Corporation of Japan

(Incorporated in Japan)

**5-2 Nagatacho 2-chome,
Chiyoda-ku, Tokyo, Japan**

**Junichi Nishizawa
6-16 Komegafukuro 1-chome,
Sendai-shi, Miyagi-ken, Japan**

Oki Electric Industry Co. Ltd

(Incorporated in Japan)

**7-12 Toranomom 1-chome,
Minato-ku, Tokyo, Japan**

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H1K 1AA9 1CA 1CB 2R3A 2R3E 2S19 2S1C 2S1D
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(72) Inventors

**Junichi Nishizawa
Hitoshi Abe**

(74) Agent and/or Address for Service

**Venner Shipley & Co
368 City Road, London, EC1V 2QA**

(54) **Growth of doped semiconductor monolayers**

(57) Doped molecular layer epitaxy of a compound semiconductor eg GaAs is achieved by the individual steps of introducing and evacuating a first source gas, introducing and evacuating a second source gas, and introducing and evacuating an impurity gas which contains an impurity element. The doped impurity concentration varies almost linearly with the pressure during doping in a wide range.

FIG. 1

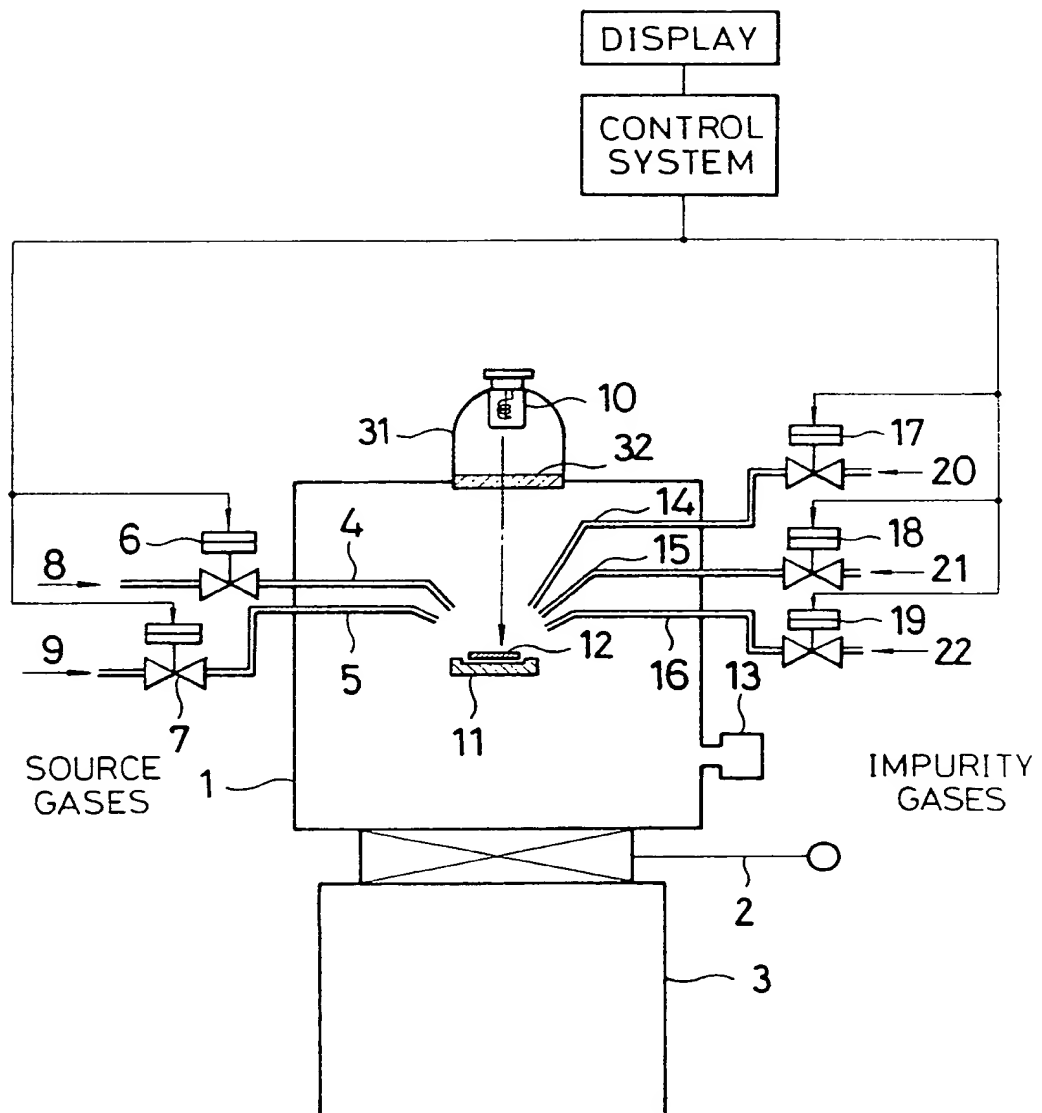


FIG. 2

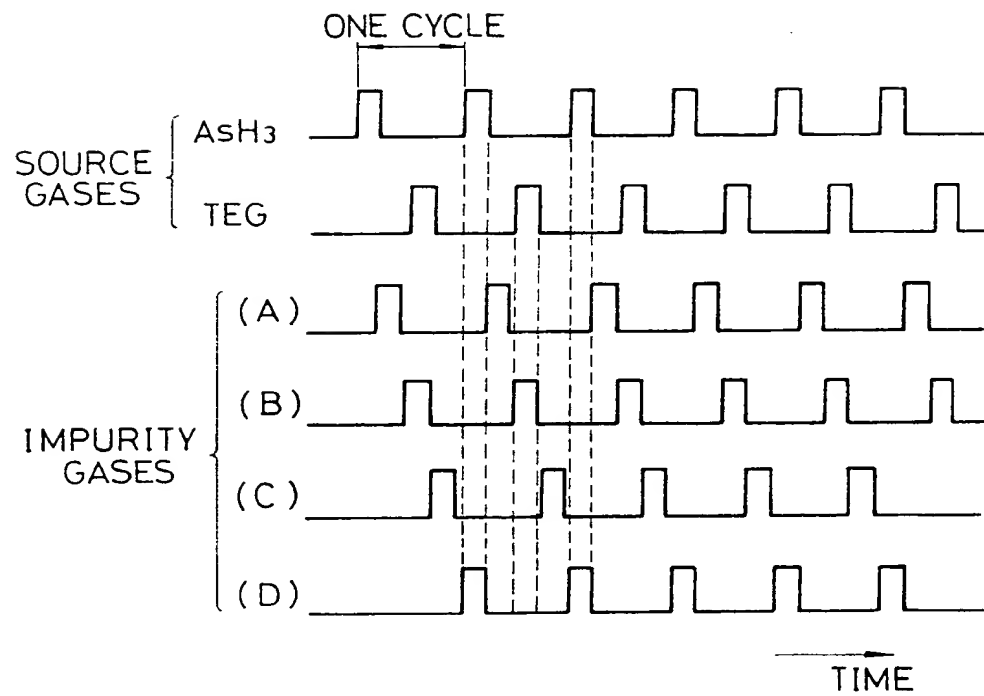


FIG. 3

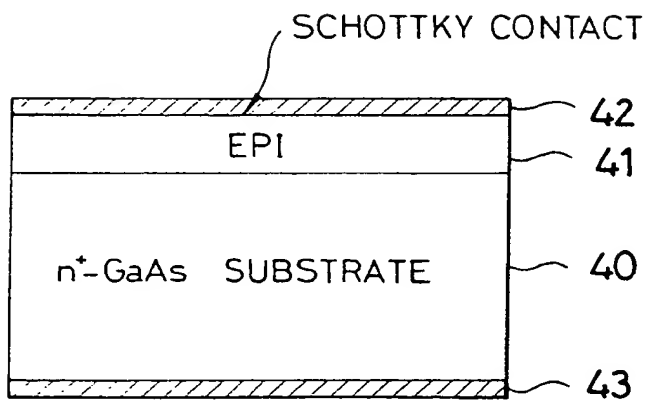


FIG. 4

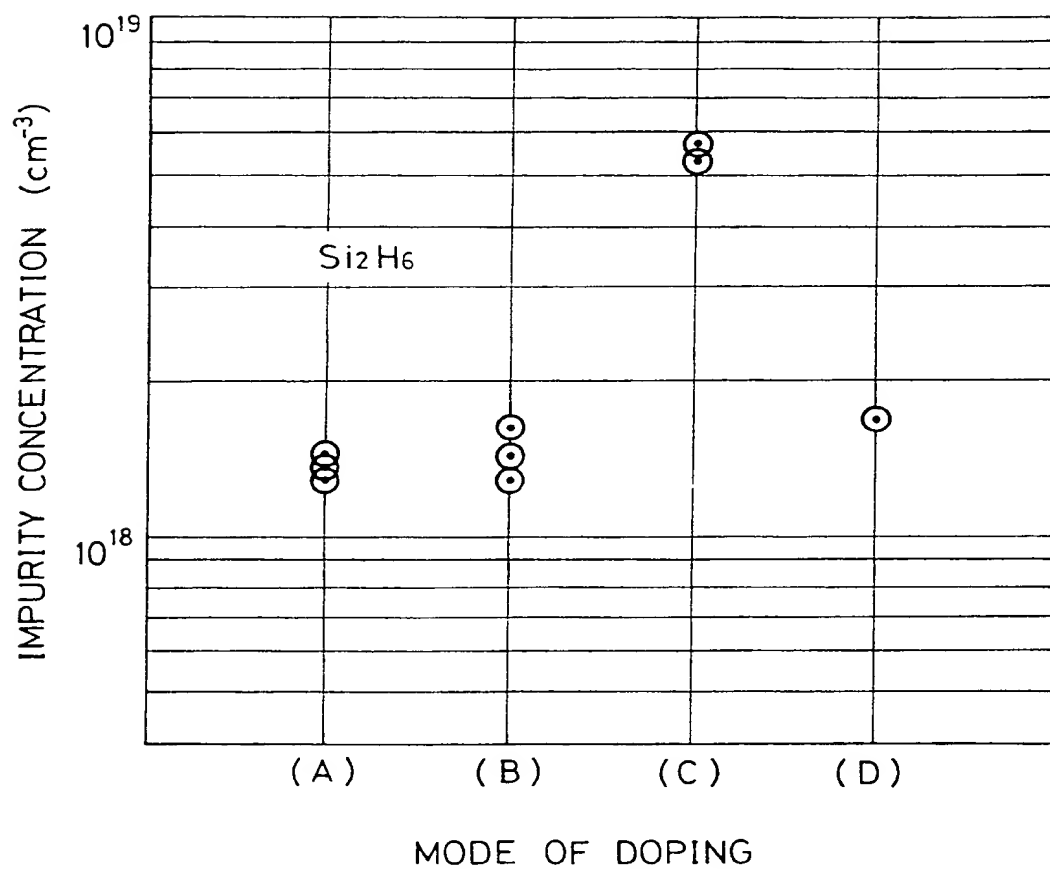


FIG. 5

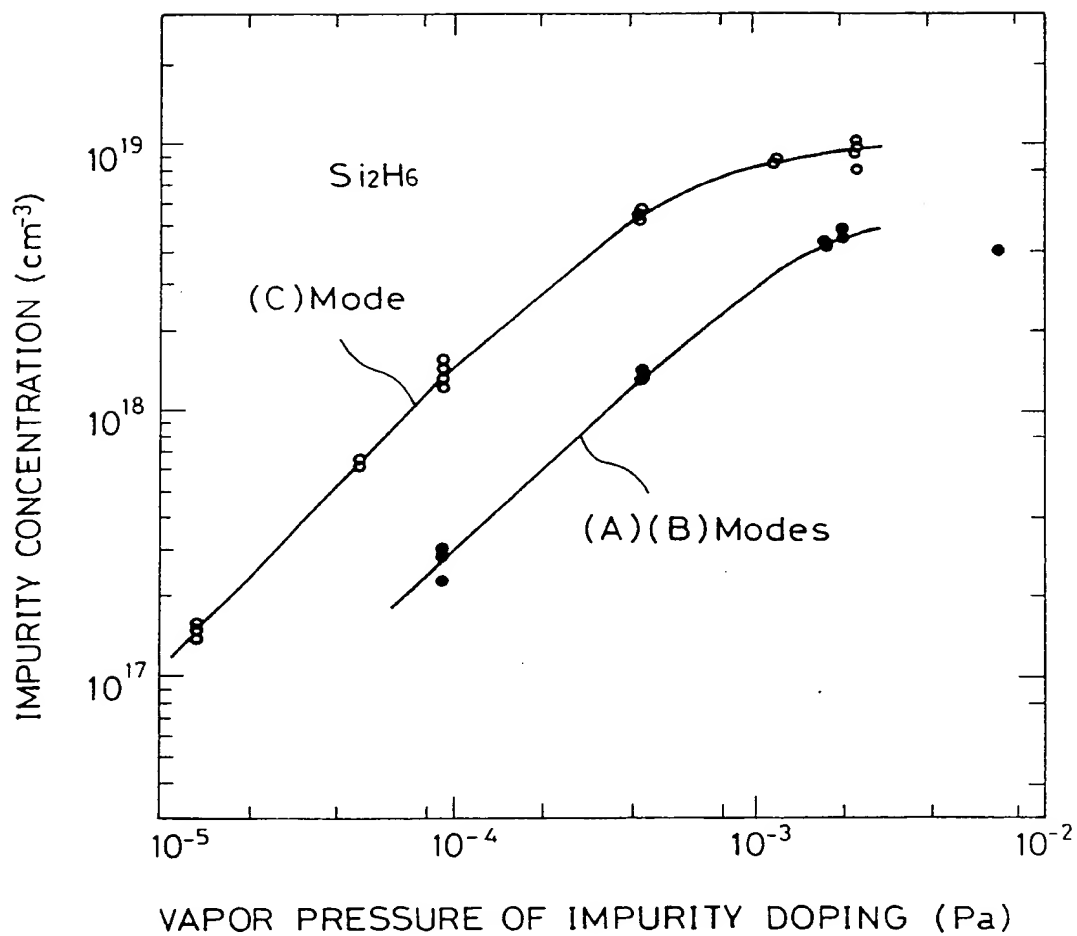


FIG. 6

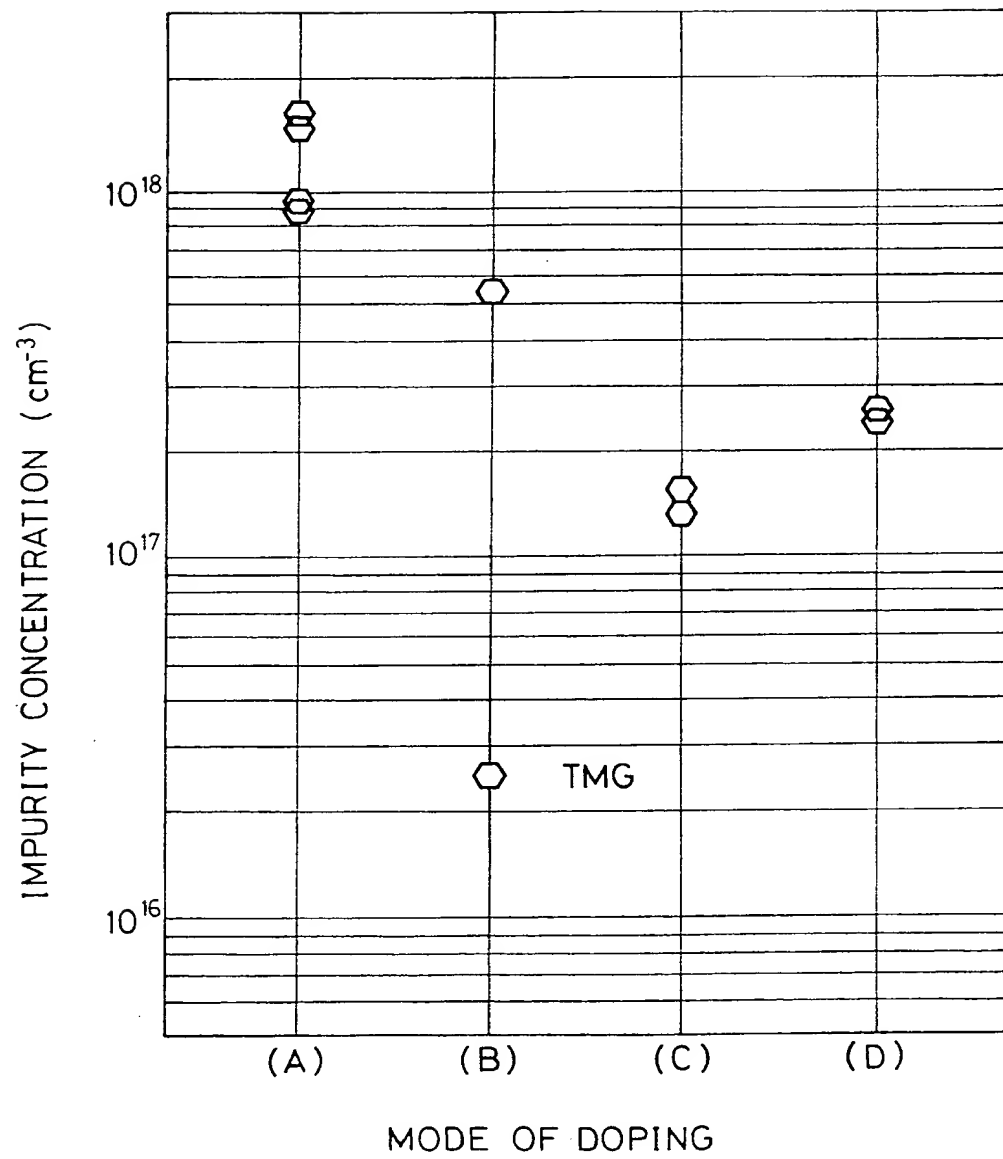


FIG. 7 A

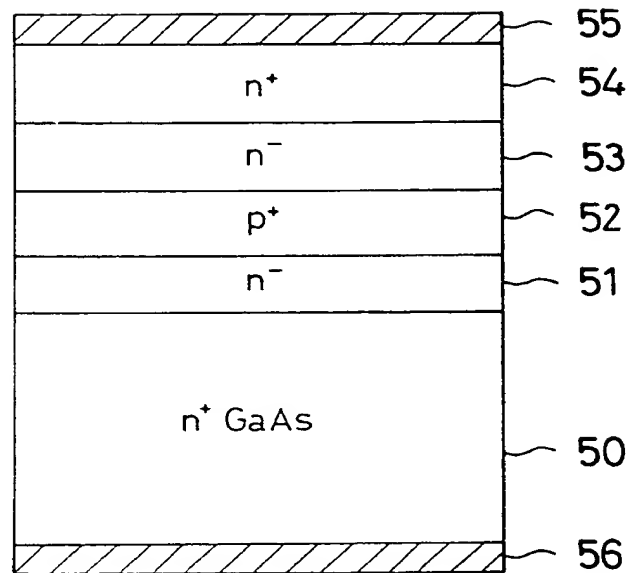
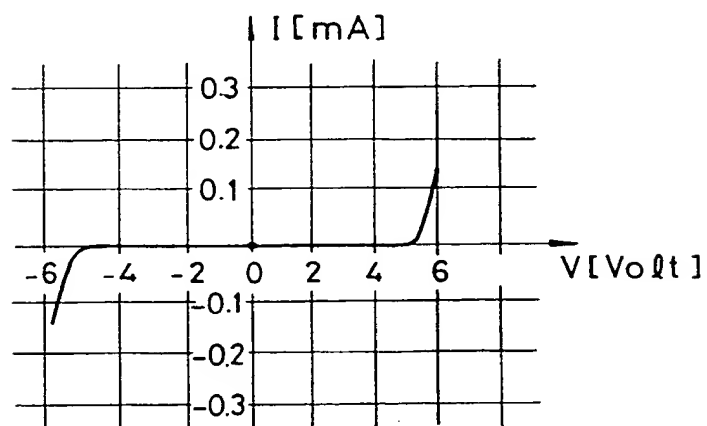


FIG. 7 B



GROWTH OF DOPED SEMICONDUCTOR MONOLAYERS

BACKGROUND OF THE INVENTION

2198152

Field of the Invention

This invention relates to growth of doped single crystal semiconductor films and more particularly to growth of doped compound semiconductor monolayers. In this specification, the term "monolayer" will mean mono-molecular layer.

Description of the Related Art

Organo-metal chemical vapor deposition (OMCVD or MOCVD), molecular beam epitaxy (MBE), etc. are known as the vapor phase epitaxial growth techniques for growing semiconductor single crystal thin films.

For example, in an example of MOCVD for growing a group III-V compound semiconductor single crystal thin films, an organo-metal gas containing a group III element and a gas containing a group V element are simultaneously introduced into a reaction chamber with H_2 gas or the like serving as a carrier gas, thereby growing group III-V compound semiconductor single crystal thin films on a substrate crystal through chemical reaction. Since a large quantity of source gases co-exist in a reaction chamber, this method is fitted for mass production. The thickness control of grown film at the monolayer order, however, is not easy.

According to MBE, a molecular beam is formed by

evaporation or the like in an ultra-high vacuum and directed to a substrate crystal producing deposition of a single crystal film on the substrate crystal. The thickness control of the grown crystal at the monolayer order can be achieved in this method. The crystal growth by MBE, however, involves physical adsorption as the first step, which may lead to inferior crystallinity to that obtainable by CVD utilizing chemical reaction. In growing a group III-V compound semiconductor crystal, such as GaAs, a group III element and a group V element are used as sources or raw materials. Solid source materials may directly be set in a reaction chamber and heated to generate vapor phase sources. The control of evaporation and the feed of additional source materials, however, are not easy. Thus, it is rather difficult to keep the growth rate at a constant value for a long period. For exhausting the waste vapors to keep the ultra high vacuum, there are restrictions on the evacuation system. Also, it is not easy to precisely control the stoichiometric composition of the compound semiconductor. Thus, it is not easy to obtain crystals of high quality by MBE. Part of the present inventors have proposed a method of growing semiconductor crystals, which is named molecular layer epitaxy, with film thickness controllability of the order of monolayers (Japanese Patent Application 59-153978 which is published as Laid-Open 61-34928, and corresponding to US patent application Serial No. 759,098, which is incorporated herein by reference).

For making various semiconductor devices such as bipolar transistors, field effect transistors, static induction transistors, etc., it is desired to grow epitaxial multi-layer structures having sharp impurity concentration profiles of npn, npin, pnp, pnip, n^+in , $n^+n^-n^+$, etc. It is strongly desired to control the impurity concentration in n- and p-type grown layers arbitrarily. Also, the miniaturization or scaling-down of a transistor is desired to achieve high speed and low power dissipation operation and high integration density. As the scaling down proceeds, the width of the conducting members becomes small. For forming good electrodes or contacts, it is necessary to make the contact resistance small and the current density per unit area large. For such usages, semiconductor regions of very high impurity concentrations (n^+ or p^+) are desired.

According to the growth method proposed by part of the present inventors as referred before, the control of impurity concentration was not always good. For example, a non-doped (not intentionally doped) GaAs film might have a p type impurity concentration of 10^{18} to 10^{20} cm^{-3} .

Improvement in control of impurity doping has been desired.

SUMMARY OF THE INVENTION

An object of this invention is to provide a method for growing semiconductor single crystal films having arbitrarily selected impurity concentrations under the thickness control of monolayer order.

Another object of this invention is to provide a

method for growing doped monolayers of compound semiconductor under high controllability.

. According to an aspect of this invention, in molecular layer epitaxy of compound semiconductor, the timing of impurity doping is selected to achieve high crystallinity of the grown layer and a desired impurity concentration.

In a case of growing III-V compound semiconductor monolayers by repeating alternate deposition of group III atomic layer and group V atomic layer, an impurity containing gas is preferably introduced after a pair of group III atomic layer and group V atomic layer are formed. For example, first a group III gas is introduced, second a group V gas is introduced and then an impurity gas is introduced. In molecular layer epitaxy of group III-V compound semiconductor, it is considered that each constituent atomic layer is preferentially deposited on the substrate crystal having a surface atomic layer of the other species. Impurity is preferably doped between the formations of adjacent atomic layers or monolayers.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram of a system for growing crystals for use in an embodiment of the present invention.

Fig. 2 is a timing chart for feeding source gases and an impurity gas in four modes of doping.

Fig. 3 is a cross-section of a semiconductor diode

fabricated for the purpose of measuring thickness of the grown film.

Fig. 4 is a graph showing the relation between the mode of doping di-silane (Si_2H_6) and the impurity concentration in the doped grown layer.

Fig. 5 is a graph showing the relation between the vapor pressure of impurity gas during doping and the impurity concentration in the doped grown layer for the modes of doping C and A&B.

Fig. 6 is a graph showing the relation between the mode of doping tri-methyl-gallium (TMG) and the impurity concentration in the doped grown layer.

Fig. 7A is a cross-section of a semiconductor diode formed to have predetermined impurity concentration distribution according to an embodiment of the invention.

Fig. 7B is a graph showing the current (I) versus voltage (V) characteristic of a diode of Fig. 7A.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now, the present invention will be described in more detail referring to the preferred embodiments.

Fig. 1 shows a structure of a system of molecular layer epitaxy to be used in an embodiment of the invention.

In the figure, reference numeral 1 denotes a growth or reaction chamber formed of a metal such as stainless steel, 2 a gate valve, 3 an evacuation system for evacuating the growth chamber 1 to an ultra high vacuum through the gate valve 2, 4 and 5 nozzles for introducing

gaseous compounds containing constituent elements, such as group III and group V elements in a case of group III-V compound semiconductor, 6 and 7 valves for opening and closing the feed path for the gaseous compounds led to the nozzles 4 and 5, 8 a gaseous compound containing a group III constituent element, 9 a gaseous compound containing a group V constituent element, 10 a heater for heating a substrate exemplified as a quartz glass sealed tungsten (W) lamp, 11 a susceptor for mounting a substrate or substrates, 12 a substrate of a compound semiconductor, 13 a pressure or vacuum gauge for measuring the pressure or vacuum in the growth chamber, 14, 15 and 16 nozzles for introducing gaseous compounds used for impurity doping, 17, 18 and 19 valves for opening and closing the feed paths for the gaseous compounds led to the nozzles 14, 15 and 16, 20 a gaseous compound containing a group II element, 21 a gaseous compound containing a group IV element, 22 a gaseous compound containing a group VI element, 31 a lamp chamber for containing the heater lamp 10, and 32 a radiation transmitting window formed of quartz glass.

Shortly, the growth chamber 1 is provided with the vacuum system 3 for maintaining an ultra high vacuum, the radiation source 10 for heating the substrate 12, and nozzles 4, 5, 14, 15 and 16 for feeding the constituent elements of the compound semiconductor and the impurity to be doped.

Monolayers of GaAs, for example, can be

epitaxially grown on the substrate 12 in a following manner.

First, the gate valve 2 is opened and the growth chamber 1 is evacuated by the ultra high evacuation system 3 to a vacuum of the order of 10^{-7} to 10^{-8} Pa. Next, the GaAs substrate 12 is heated by the heater 10 to a temperature of about 300 to 800°C, for example. Then, tri-methyl-gallium (TMG) 8 as a Ga-containing gas is introduced into the growth chamber 1 at a pressure of 10^{-1} to 10^{-7} Pa for 0.5 to 10 seconds by opening the valve 6. Thereafter, the valve 6 is closed and the residual gas in the growth chamber 1 is evacuated. Then, arsine (AsH_3) 9 as an As-containing gas is introduced into the growth chamber 1 at a pressure of 10^{-1} to 10^{-7} Pa for 2 to 200 seconds by opening the valve 7. Thereafter, the valve 7 is closed and the chamber 1 is evacuated to recover an ultra high vacuum. The above steps will constitute one cycle of growing one monolayer of GaAs on the substrate 12. By repeating the above-mentioned cycles, monolayers of GaAs can be successively grown to a desired thickness to form an epitaxial GaAs layer having a thickness controlled to the accuracy of monolayer order.

Now, doped epitaxial growth will be explained taking GaAs as an example. Arsine (AsH_3) may be used as an As-containing gas and tri-ethyl-gallium (TEG) may be used as a Ga-containing gas. TEG has an advantage of achieving a lower temperature growth and a lower background impurity concentration compared to TMG. Thus, epitaxially grown films of excellent crystallinity and a low impurity

concentration of 10^{15} cm^{-3} or less could be grown.

Now, molecular layer epitaxy with n-type impurity doping, using AsH_3 and TEG as the source gases and Si_2H_6 as the dopant gas, will be described. Silicon atom (Si) enters a Ga site substitutionally and becomes an n-type impurity. When the impurity gas is introduced selectively on the time axis, typically following four modes of doping can be considered:

- (A) at the exhaustion of AsH_3 ,
- (B) at the introduction of TEG,
- (C) at the exhaustion of TEG, and
- (D) at the introduction of AsH_3 .

Fig. 2 illustrates these four modes of doping the impurity in a timing chart. One of the timings A, B, C and D will be selected as the mode of doping. Except the impurity doping, AsH_3 and TEG are alternately introduced and exhausted. One cycle of AsH_3 and TEG will form one monolayer. In accompanying with the monolayer growth, impurity is doped once a cycle. The timing of impurity doping is set at the above-mentioned four modes A, B, C and D.

In a cycle, AsH_3 gas was introduced at 4.2×10^{-2} Pa for 10 seconds, TEG was introduced at 2.4×10^{-4} Pa for two seconds, and Si_2H_6 was introduced at 8.6×10^{-5} Pa. Conditions of film formation were kept same for the four modes of doping except the timing of doping Si_2H_6 . Substrate temperature was kept at about 380°C . After the

film formation, electrical properties and C-V (capacitance vs. voltage) characteristics were measured. It was confirmed that one monolayer (2.83\AA thick) was grown substantially in one cycle. The samples were made in the form of a diode as shown in Fig. 3 for use in electrical measurement.

In Fig. 3, reference numeral 40 denotes an n^+ substrate, 41 a film epitaxially grown on the substrate 40 while being doped, 42 a metal layer deposited on the grown film for making a Schottky contact, and 43 a metal film forming an ohmic contact with the n^+ substrate. The C-V characteristics of this diode was measured and the spreading of the depletion layer was calculated. Then, the thickness of the epitaxially grown layer 41 can be calculated. In this way, it was confirmed non-destructively whether the epitaxial growth is effected monolayer by monolayer.

Fig. 4 shows the impurity concentration in the epitaxial films grown under the above-mentioned conditions and doped with impurity in the modes of doping A, B, C and D. The impurity concentration was derived from the Hall effect measurement. In the mode C where doping is done when TEG is exhausted, the impurity concentration was $5.6 \times 10^{18} \text{ cm}^{-3}$, which is about four times as large as the impurity concentrations $n = 1.4 \times 10^{18} \text{ cm}^{-3}$ for other three modes. It is known from this fact that doping efficiency is very high for the mode C. In this case, the order of gas introduction or gas feed is (group V, group III, group IV)

or (group III, group IV, group V) which can be expressed as from the low group to the high group in the periodic table, to achieve growth of each doped monolayer.

Next, the conditions for introducing AsH_3 gas and TEG gas were set at constant and the quantity (i.e. pressure) of doping Si_2H_6 was varied. The obtained impurity concentrations or carrier concentrations are shown in Fig. 5. The carrier concentration increases almost linearly with the increase in the dopant (Si_2H_6) pressure, but is saturated around a certain value. The controllability of doping impurity by the dopant pressure was very good and a good linearity was obtained over three orders of magnitudes, in the range of 10^{15} to $4 \times 10^{18} \text{ cm}^{-3}$. Further, in the mode C, the saturation value was about $1 \times 10^{19} \text{ cm}^{-3}$, which is more than twice the values for the other modes. Furthermore, the surface of the grown layer according to mode C was mirror-like, while the surfaces of the grown layers for the other modes were roughened to some extent. Comparing the characteristics of the samples having an impurity concentration of $2 \times 10^{18} \text{ cm}^{-3}$ and doped by the four modes, the mobility of carriers for the crystal doped by the mode C was $\mu_n = 1600 \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$, while the mobility in the samples doped by the other modes was about $\mu_n = 1300 \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$. The sample doped by the mode C had the most preferable characteristics from the viewpoints of crystal surface morphology and carrier mobility.

From these results, it was found, in the case of a

dopant gas Si_2H_6 , that good crystals were obtained when the impurity is doped at a timing when group III and V elements are exhausted.

Next, p type doping using TMG as the impurity gas will be described.

In molecular layer epitaxy employing alternate introduction of AsH_3 and TMG, p-type epitaxial layers have been obtained which have impurity concentration ranging from 10^{18} to 10^{20} cm^{-3} . Such p-type layers have good crystallinity and are suited for use as heavily doped p^+ -type layers. From the measurements of secondary ion mass spectroscopy (SIMS), etc., the impurity element in the grown layer is considered to be the carbon atom entered substitutionally in the group V, i.e. As, site. Thus, TMG can be considered to be the impurity gas for doping carbon atoms, which are the p-type impurity element in the GaAs crystal. Then, TMG is doped in the monolayers epitaxy of (AsH_3 , TEG). The growth conditions were selected the same as those for doping Si_2H_6 . The period of introducing TMG was set at 2 seconds and the quantity of dopant (pressure) was varied.

The p-type impurity concentration could also be well varied in the range of 10^{15} to $5 \times 10^{18} \text{ cm}^{-3}$ with good controllability.

In an example, the pressure of TMG in doping was set at $2.1 \times 10^{-4} \text{ Pa}$, the period of doping was set at 2 seconds, and the conditions of introducing AsH_3 and TEG

etc. were selected the same as those in the embodiment of Fig. 4. The mode dependency of doping obtained in this case is shown in Fig. 6. The lower mark on axis B is not a data but a legend. The doping efficiency was the highest for the mode A and was low for the mode C. This mode dependency of the doping efficiency is a reversed one to that for the case of doping Si_2H_6 . In this p-type doping, the best doping efficiency is considered to be obtained when molecular layer epitaxy is achieved by introducing (group III - group V) elements and then the impurity gas of group IV, carbon, in this order. From the Hall mobility and the surface morphology, modes A and C were found to be better than other modes B and D.

Then, doping of impurity gases of group II and group VI elements were carried out. Using di-methyl-cadmium (DMCd) as an impurity gas, p type layers having an impurity concentration in the range of 10^{15} to $1 \times 10^{18} \text{ cm}^{-3}$ were formed with good controllability. Doping was better effected when the impurity gas containing group II element is introduced when group III or V element is exhausted. In the case of H_2Se (hydrogen selenide), the impurity concentration could only be controlled in the range of 10^{18} to $2 \times 10^{19} \text{ cm}^{-3}$ due to the memory effect. In the case of di-ethyl-selenium (DESe), the impurity concentration could be controlled in a wide range of 10^{15} to $2 \times 10^{19} \text{ cm}^{-3}$. In this case, impurity was better doped when doped after the exhaustion of group V element. Also in doping group II or

VI impurity, modes A and C, where impurity gas is introduced when group III or V element has been exhausted, were found to be preferable from the points of good surface morphology, higher carrier mobility, and good crystallinity. The mode dependency of doping efficiency for these impurity gases was tested under the same conditions of forming GaAs layer as those for the case of Si_2H_6 doping. It was found that the doping efficiency has the following characteristic.

Taking GaAs as an example, it was found that the doping efficiency becomes the maximum to achieve a higher impurity concentration when an impurity containing gas is introduced at the exhaustion after the introduction of Ga or As containing gas. When a group IV element is used as an n-type impurity, the doping efficiency is high when gas introduction is in the order of (III-V)-VI or (V-III)-VI. When a group II element is used as a p-type element, the doping efficiency is high when gas introduction is in the order of II-(III-V) or II-(V-III).

Description will now be made on diodes made through the impurity doping in molecular layer epitaxy as described above. In Fig. 7A, on an n^+ -type GaAs substrate 50, an n^- -type layer 51, a p^+ -type layer 52, a n^- -type layer 53 and an n^+ -type layer 54 of respective predetermined impurity concentration and thicknesses of 300, 300, 300 and 600 monolayers were epitaxially grown successively. Thereafter, AuGe/Au layer is deposited on the both surfaces and sintered at 350°C in N_2 atmosphere to form good ohmic

contacts 55 and 56 according to the ordinary diode manufacture. The electrode area was selected to be 300 μm square. The I-V characteristics of the obtained diode are shown in Fig. 7B. The characteristics are good with a breakdown voltage of more than 5 volts

In the above description, this invention has been explained taking mainly doping of GaAs as examples. It will be without saying that the invention is also applicable to other III-V compound and mixed crystal semiconductors such as InP, GaP, GaAlAs, InGaAlAsP and to other compound semiconductors. As the gases containing group III element or group V element, those gases such as tri-methyl-indium (TMIn), tri-ethyl-indium (TEIn), tri-isobutyl-indium (TIIn), phosphine (PH_3), tri-methyl-aluminium (TMAI), tri-ethyl-aluminium (TEAI), and tri-isobutyl-aluminium (TIAI) may be used. As the impurity gas, those gases as described hereinabove which contain group II, group IV or group VI element may be used. Impurity doping in a wide range of 10^{15} to $5 \times 10^{18} \text{ cm}^{-3}$ could be carried out with good controllability while maintaining the features of molecular layer epitaxy.

As described above, according to the present invention, molecular layer epitaxy can be achieved at a low temperature with controlled doping for each monolayer. Very sharp impurity concentration distribution can be formed according to the designed value. By the selection of doping timing, the doping efficiency can be increased and the

maximum impurity concentration will be raised.

Particularly, when the impurity is introduced after the exhaustion of a gas containing a group III or V element, the surface state and the crystallinity were found to be good. Formation of heavily doped high quality layers required for high speed/high integration devices can be achieved easily at a low temperature with thickness control of monolayer order. Therefore, this invention exhibits excellent functions and effects in the formation of devices which require extreme size accuracy.

CLAIMS:

1. A method of forming a doped compound semiconductor single crystal layer comprising the steps of:
 - (a) evacuating a growth chamber to a predetermined pressure;
 - (b) heating a crystal substrate disposed in the growth chamber to a predetermined temperature;
 - (c) introducing a first source gas containing one constituent element of said compound into said growth chamber and onto said substrate;
 - (d) evacuating the growth chamber to exhaust the waste first source gas;
 - (e) introducing a second source gas containing another constituent element of said compound into said growth chamber and onto said substrate;
 - (f) evacuating the growth chamber to exhaust the waste second source gas;
 - (g) repeating cycles each including said steps (c), (d), (e) and (f) to grow monolayers on said substrate; and
 - (h) doping impurity gas into said growth chamber after step (d) or (f) in each cycle.
2. A method of forming a doped compound semiconductor single crystal layer according to claim 1, wherein said compound is a group III-V compound.
3. A method of forming a doped compound semiconductor single crystal layer according to claim 2,

wherein said impurity gas contains an element belonging to one of group II, group IV and group VI of the periodic table and the steps (c), (e) and (h) are so ordered that the group of the element contained in the gas increases from a small value to a large value.

4. A method of forming a doped compound semiconductor single crystal layer according to claim 2, wherein the compound is GaAs.

5. A method of forming a doped compound semiconductor single crystal layer according to claim 2, wherein said impurity gas is one of di-methyl-cadmium (DMCd), Si_2H_6 , tri-methyl-gallium (TMG), di-ethyl-selenium (DESe), and H_2Se .

6. A method of forming a doped compound semiconductor single crystal layer according to claim 2, wherein said impurity gas contains silicon serving as an n-type impurity, and said step (h) is carried out after said step (f) which exhausts waste second source gas which contains gallium.

7. A method of forming a doped compound semiconductor single crystal layer according to claim 2, wherein said impurity gas contains carbon serving as a p type impurity and said step (h) is carried out after said step (d) which exhausts waste first source gas which contains arsenic.

8. A method of forming a compound substantially as herein described with reference to the accompanying drawings.

5 9. A doped compound formed by a method according to any preceding claim.

10 10. Apparatus for forming a doped compound according to a method as claimed in any one of claims 1 to 8.